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(54) Title: DEODORANT POLYMER FILM AND SHEET FORM DEODORIZER <div data-bbox="368 1108 1148 1415" data-label="Image"> </div> (57) Abstract A deodorant polymer film comprising: (a) 30 to 100 % by weight of a deodorant polymer obtained by polymerization of monomer components comprising 10 to 99 % by weight of a deodorant ethylenically unsaturated monomer having a deodorant functional group in the molecule, and 1 to 90 % by weight of a hydrophilic ethylenically unsaturated monomer having no deodorant functional group; and (b) 0 to 70 % by weight of water which is in the compatible state with the deodorant polymer, wherein said deodorant polymer is cross-linked and said polymer film is solid at ambient temperature.		

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## DEODORANT POLYMER FILM AND SHEET FORM DEODORIZER

### Field of the Invention

5 The present invention relates to a deodorant polymer film and a sheet form deodorizer comprising the same, which manifests deodorant action by catching an odor substance. The deodorant polymer has a deodorant functional group such as an acidic functional group, and demonstrates a deodorant action by catching and neutralizing an odor substance. In general, the deodorant polymer film comprises a deodorant substance and water which is in contact with the deodorant substance.  
10 Water may be supplied by including water in the deodorant polymer film, or by including a hydrophilic component having moisture absorptivity in the deodorant polymer film.

### Background of the Invention

15 Japanese laid open publication 237924/1987 discloses a deodorizer using a cation exchange fiber to which a sulfonic group is introduced by sulfuric acid treatment of the surface of a hydrophilic polymer fiber formed by using polyvinyl alcohol as a starting material. In a deodorant method utilizing a neutralization reaction, an increased amount of a deodorant functional group is necessary to promote deodorant action. In a deodorizer containing a deodorant substance in its fiber surface, the amount of the fiber also is necessary to be increased for increase of the amount of the deodorant functional group. Consequently, the deodorizer having high deodorant action inevitably becomes bulky. When such a bulky deodorizer is placed in a relatively narrow restricted accommodation space such as  
20 a refrigerator, cabinet, shoe box or the like, utilization of the accommodation space becomes ineffective. Further, in deodorizing an odor in a vessel such as a garbage can, toilet bowl or the like, it is difficult to place a deodorant material near an odor source to enhance deodorizing effect without disturbing the use thereof.

25 Japanese laid open publication 239504/1992 discloses a deodorizer comprising an aqueous gel containing 20% by weight of a hydrophilic polymer and a low molecular weight deodorant substance. This deodorizer must retain as much  
30

water as possible to increase deodorant substance content. Therefore, the above-mentioned aqueous polymer is in the form of a jelly, and the content of the hydrophilic polymer in the gel is low. On the other hand, to effectively catch the odor substance floating in a vapor such as air, it is necessary to increase the contact area with the vapor. Since the above-mentioned aqueous gel is not fully crosslinked and is in the form of a jelly and has poor molding ability, for example, when it is molded even in the form of a film, it can not maintain its form. Therefore, to increase the contact area with a surrounding vapor, an aqueous gel is necessary to increase its volume. Then, the jelly form deodorizer as described above also becomes bulky to enhance the deodorant effect as in the case of the fibrous deodorizer. Therefore, it is difficult to utilize effectively an accommodation area, and to enhance the deodorant effect by placing a vessel containing a deodorizer near an odor source.

#### **Summary of the Invention**

The present invention solves the above-mentioned problems, and an object thereof is to provide a deodorant polymer film and a sheet form deodorizer, which enhance deodorant effect when placed near an odor source.

The present invention provides a deodorant polymer film comprising: (a) 30 to 100% by weight of a deodorant polymer obtained by polymerization of monomer components comprising 10 to 99% by weight of a deodorant ethylenically unsaturated monomer having a deodorant functional group in the molecule, based on the total weight of the deodorant polymer film and 1 to 90% by weight of a hydrophilic ethylenically unsaturated monomer having no deodorant functional group, based on the total weight of the deodorant polymer film; and (b) 0 to 70% by weight of water; wherein said deodorant polymer is crosslinked and said polymer film is solid at ambient temperature.

#### **Brief Description of the Drawings**

Fig. 1 is a cross sectional view showing one embodiment of the sheet form deodorizer of the present invention.

Fig. 2 is a perspective view showing one embodiment of the sheet form deodorizer of the present invention.

#### **Detailed Description of the Invention**

5 In the present specification, the term "monomer" such as in "deodorant ethylenically unsaturated monomer", "hydrophilic ethylenically unsaturated monomer having no deodorant functional group" and "monomer having more than one ethylenically unsaturated bond", means a general term of a polymerizable compound having at least one ethylenically unsaturated bond in the molecule.  
10 Namely, the term "monomer" includes an oligomer and a polymer as well as a conventional low molecular weight monomer. Preferred examples of the monomers are described below.

The deodorant polymer film of the present invention comprises a deodorant polymer, and optionally, water which is compatible with the deodorant polymer.

15 The deodorant polymer is a copolymer of a monomer mixture which contains a deodorant ethylenically unsaturated monomer as an essential component, and optionally, contains a hydrophilic ethylenically unsaturated monomer having no deodorant functional group.

The term "deodorant ethylenically unsaturated monomer" means a monomer  
20 containing a deodorant functional group and an ethylenically unsaturated bond in the molecule. This is a compound generally having a molecular weight of from 65 to 1,000, preferably from 70 to 300.

The term "deodorant functional group" means a functional group which manifests deodorant action by catching and neutralizing the odor substance. In  
25 general, this functional group is an acidic functional group when the odor substance is a basic substance, and is a basic group when the odor substance is an acidic substance. For example, when the odor substance is a basic amine compound, a sulfonic group, phosphoric group, carboxyl group and a metal salt thereof is effective as the deodorant functional group. When the functional group forms a  
30 metal salt, a metal such as copper, iron, zinc or the like is generally used. Further, if

the odor substance is a carboxylic acid, an amino group is effective as the deodorant functional group.

Examples of the deodorant ethylenically unsaturated monomer include 2-(meth)acrylamide-2-methylpropanesulfonic acid, (meth)acrylamidealkylsulfonic acid, styrenesulfonic acid, 2-(meth)acryloxyethyl phosphate and metal salts thereof. (Meth)acrylamidealkylsulfonic acid such as 2(meth)acrylamide-2-methylpropanesulfonic acid is particularly preferable.

To prepare the deodorant polymer of the present invention, the deodorant ethylenically unsaturated monomer is used in an amount of from 10 to 99% by weight, preferably from 12 to 90% by weight, further preferably from 15 to 80% by weight. Deodorant ability begins to lessen when the amount of the deodorant ethylenically unsaturated monomer is less than 10% by weight.

The term "hydrophilic ethylenically unsaturated monomer having no deodorant functional group" means a monomer having a hydrophilic moiety other than a deodorant functional group and an ethylenically unsaturated bond in the molecule. This is a compound which, when incorporated in a deodorant polymer molecule, allows the deodorant functional group coexisting in the same molecule to constantly contact water (such as moisture from air, or the like) and to assist in neutralization of the odor substance effectively. The hydrophilic ethylenically unsaturated monomer having no deodorant functional group is a compound generally having a molecular weight of from 65 to 1,500, preferably from 70 to 1,300.

Specific examples of the hydrophilic moiety include a hydroxyl group, polyethylene glycol moiety, amino group, amide group, carboxyl group and the like. A preferable hydrophilic moiety is a nonionic moiety which substantially does not ionically dissociate when dissolved in water such as a polyethylene glycol moiety or amide group.

Examples of the hydrophilic ethylenically unsaturated monomer having no deodorant functional group include methyl polyethylene glycol (meth)acrylate having a number average molecular weight of about 200 to 800, 4-hydroxybutyl (meth) acrylate, acrylamide, N,N-dimethyl acrylamide, polyvinyl alcohol having a

(meth)acrylic group in the molecule, and the like. Particularly preferably are methyl polyethylene glycol (meth)acrylate having a number average molecular weight of about 400 to 600, particularly about 490, 4-hydroxybutyl (meth)acrylate, acrylamide and N,N-dimethyl acrylamide.

5 To prepare the deodorant polymer of the present invention, the hydrophilic ethylenically unsaturated monomer having no deodorant functional group is used in an amount of from 1 to 90% by weight, preferably from 5 to 85% by weight, more preferably from 10 to 80% by weight. When using the hydrophilic ethylenically unsaturated monomer having no deodorant functional group in an amount less than  
10 1% by weight, water absorption ability may lower which decrease deodorant ability, and when using the hydrophilic ethylenically unsaturated monomer having no deodorant functional group in an amount over 90% by weight, the concentration of the deodorant functional group is lowered which may lessen deodorant ability. Further, when the amount of the monomer is too low, flexibility of the film may be  
15 lowered, or applicability of the monomer mixture may be lowered.

If the flexibility of the film becomes poor, the process for cutting, or bending it becomes difficult. If the applicability of the monomer mixture becomes poor, inconveniences such as cissing may occur which disturbs the formation of an applied film.

20 The hydrophilic ethylenically unsaturated monomer having no deodorant functional group and the deodorant ethylenically unsaturated monomer are copolymerized according to the process described below, to form the deodorant polymer.

It is preferable that the deodorant polymer of the present invention is a  
25 crosslinked polymer. Crosslinking of the deodorant polymer raises mechanical strength of the deodorant polymer after polymerization, to enable maintenance of film form. Further, when water is included in the deodorant polymer film, water retention ability is enhanced, and elapsed stability of deodorant action is raised.

To crosslink the deodorant polymer, a monomer generally having more than  
30 one ethylenically unsaturated bonds in the molecule (hereinafter, referred to as

"crosslinking monomer") is used. A crosslinking monomer is a compound generally having a molecular weight of from 150 to 1,500, preferably from 170 to 1,300.

Examples of the crosslinking monomer include 1,6 - hexanediol diacrylate, diethylene glycol di(meth)acrylate and polyethylene glycol di(meth)acrylate.

5 Particularly preferable examples include 1,6-hexane diol diacrylate and diethylene glycol di(meth)acrylate.

The crosslinking monomer is used in an amount of from 6.1 to 10 parts by weight, preferably from 0.2 to 7 parts by weight, more preferably from 0.5 to 5 parts by weight based on 100 parts by weight of the deodorant polymer. When the  
10 amount of crosslinking monomer is less than 0.1 parts by weight, the strength of the deodorant polymer begins to lower, thus making it difficult to mold the polymer in the form of a film. When the amount of crosslinking monomer is over 10 parts by weight, there is a possibility that deodorant action may be lowered.

Though the crosslinking monomer may be added to a monomer mixture  
15 during polymerization of the deodorant polymer, the crosslinking monomer may also be reacted further after polymerization of the deodorant polymer.

Further, in another embodiment, the deodorant polymer may be crosslinked without using the crosslinking monomer. In such case, an ion crosslink structure is formed between the functional groups of the deodorant polymer. The ion crosslink  
20 structure means that the ionic bond through the medium of water is formed between polar groups, and the deodorant polymer is crosslinked through the ionic bond.

For example, such an ion crosslink structure is obtained when a deodorant polymer is prepared using a strong acidic monomer such as sulfonic acid or metal salt of sulfonic acid, and a suitable amount of water is included in the deodorant  
25 polymer.

In this case, the amount of water in the deodorant polymer film may range from 5 to 70% by weight, preferably 7 to 65% by weight, more preferably from 10 to 60% by weight.

Water is optionally included in the deodorant polymer film, and can promote  
30 neutralization between the deodorant functional group and the odor substance. When the deodorant polymer film is relatively thick (for example, not less than 50

μm), water help the odor substance to penetrate inside the polymer film. As a result, deodorant ability of the film is improved.

The deodorant polymer film of the present invention may contain various components as well as the deodorant polymer and water. For example, the film may contain an unpolymerizable hydrophilic substance to assist hydrophilicity of the deodorant polymer, as well as a variety of additives.

Examples of a hydrophilic substance include polyhydric alcohols such as an aliphatic alcohol having 5 to 12 carbon atoms, ethylene glycol, propylene glycol and glycerin, condensed polyhydric alcohols thereof, and surface active agents.

When the monomer mixture contains a hydrophilic substance in an amount effective for deodorizing action, the hydrophilic ethylenically unsaturated monomer having no deodorant functional group may be omitted. The hydrophilic substance is used generally in an amount of from 1 to 40% by weight, preferably from 5 to 30% by weight, based on the weight of the deodorant polymer film.

Examples of other additives include ultraviolet light absorbers, antioxidants, fillers, colorants, plasticizers, and the like.

The deodorant polymer film of the present invention can be prepared, for example, as follows. First, a monomer mixture is prepared, comprising a specific amount of a deodorant ethylenically unsaturated monomer, a hydrophilic ethylenically unsaturated monomer having no deodorant functional group, a crosslinking monomer, and other components such as an unpolymerizable hydrophilic component and various additives. The monomer mixture may also optionally include a polymerization regulator such as a photopolymerization initiator, a chain transfer agent, or a chain stopper.

A suitable amount of water may be used as the polymerization solvent. Thereby, mobility of the reactant may be retained during the polymerization, and polymerization degree of the resulting polymer can be improved. As a result, mechanical strength of the deodorant polymer film can also be improved.

Furthermore, water is harmless and does not have to be removed from the deodorant polymer film after polymerization. Also, a drying step may be omitted. Thus, employing water as the polymerization solvent, is preferred for saving cost.

Next, the monomer mixture is applied on a substrate to form a layer having a desired thickness, typically 10  $\mu\text{m}$  to 5 mm. As the substrate, a plastic film, fibrous sheet or the like may be used. Then, the applied layer is polymerized to form a deodorant polymer film.

5       The polymerization can be conducted by heating or radiation. The substrate used for molding, may be peeled off from the deodorant polymer film after polymerization, or may be retained as a supporting substrate of the sheet form deodorizer.

10       Further, for example, the monomer mixture may be impregnated into a porous sheet comprising a fiber such as a paper, unwoven fabric, towel or the like, and then polymerized to make a sheet form deodorizer.

15       In general, the deodorant polymer film of the present invention is preferably made as solid state material at normal temperature (about 250C), by a method including, for example, crosslinking at relatively high density, and decreasing the amount of solvent remaining after polymerization. Consequently, a deodorant polymer film is obtained. It can be placed at desired position without using a vessel in which the deodorizer is kept, which is different from a deodorizer in jelly form.

20       The deodorant polymer film comprises a deodorant polymer, generally in an amount of from 30 to 100% by weight, preferably from 40 to 99% by weight, more preferably from 50 to 95% by weight, based on the total weight of the deodorant polymer film. When the content of the deodorant polymer is less than 30% by weight, mechanical strength of the film may decrease, and processing or handling of the film may become difficult.

25       The deodorant polymer film preferably contains a deodorant ethylenically unsaturated monomer in an amount of from 10 to 90% by weight, preferably from 20 to 80% by weight based on the weight of the film. When the amount of the deodorant ethylenically unsaturated monomer is less than 10% by weight, deodorant ability of the deodorant polymer film may deteriorate, and when over 90% by weight, flexibility of the film may decrease and application characteristics  
30       may deteriorate.

If the amount of the ethylenically unsaturated monomer is too high, the following problems may occur. If, for example, the deodorant functional group is an acidic group such as a sulfonic group or phosphoric group and a bag in which the deodorant polymer film is kept, or a supporting substrate on which the deodorant polymer film is applied, is composed of a fibrous sheet, there is a possibility that the fibrous material may deteriorate over time. Further, when the deodorant polymer film is attached to a metal surface directly or through a relatively thin fibrous sheet, metal corrosion may occur.

The deodorant polymer film is generally formed in a thickness ranging from 10  $\mu\text{m}$  to 5 mm, preferably from 50  $\mu\text{m}$  to 4 mm. When the thickness of the deodorant polymer film is less than 10  $\mu\text{m}$ , the handling of the film may be difficult, and when it is greater than 5 mm, flexibility of the film may decrease.

The sheet form deodorizer of the present invention is obtained by applying a deodorant polymer film on a supporting substrate. The supporting substrate is used mainly for reinforcing the deodorant polymer film. For example, as the supporting substrate, a film of plastic material such as polyester, polyvinyl chloride, acrylic resin, polyurethane and polycarbonate, a metal foil such as an aluminum foil, and a fibrous sheet such as a paper, unwoven fabric, towel or the like, can be used.

The thickness of the supporting substrate can be determined based on the characteristics of the materials used. For example, in the case of a plastic film, the thickness may range generally from 10  $\mu\text{m}$  to 2 mm, preferably from 20  $\mu\text{m}$  to 1 mm. In the case of a metal foil, the thickness may range generally from 5  $\mu\text{m}$  to 1 mm, preferably from 10  $\mu\text{m}$  to 800  $\mu\text{m}$ . In the case of a fibrous sheet, the thickness may range generally from 10  $\mu\text{m}$  to 3 mm, preferably from 50  $\mu\text{m}$  to 2 mm. When the supporting substrate is too thin, the reinforcing effect is poor, and when too thick, the space saving effect may decrease.

The sheet form deodorizer of the present invention comprises the above-mentioned deodorant polymer film, and contacts a vapor (usually air) containing the odor substance at a sufficient contact area to enable the deodorant ability (for example, preferably not less than 4  $\text{cm}^2$ ). By this fact, the sheet form deodorizer manifests an excellent deodorant action in spite of a relatively low weight.

Therefore, the sheet form deodorizer of the present invention enables maximum utilization of accommodation space and enhancement of deodorant effect by placing near an odor source.

Further, since a deodorant functional group is directly bonded to the polymer molecule in the deodorant polymer film of the present invention, deodorant action is manifested stably. Namely, there is no decrease in deodorant action due to exudation or volatilization of a low molecular weight deodorant substance as occurs in the case when a low molecular weight deodorant substance is included in the deodorizer in a relatively large amount. Further, pollution of a storage place, such as the inner surface of an accommodation container, does not occur due to an exuded deodorant substance.

In a preferred embodiment of the sheet form deodorizer of the present invention, at least one main surface of the deodorant polymer film is covered with an air permeable sheet which allows the odor substance to permeate. The air permeable sheet prevents pollution of the surface of the deodorant polymer film without disturbing deodorant action of the deodorant polymer film. Further, when the deodorant polymer film contains a strong acidic or strong basic compound, the sheet form deodorizer can be used to avoid contact of the deodorant polymer film with a human body or a metal due to the presence of the air permeable sheet.

Ways to attach the air permeable sheet are well known to those skilled in the art. For example, the air permeable sheet may be attached to the deodorant polymer film, by using an adhesive or a tacky tape in the form of foam, by contact bond, by spot fusion bond by ultrasonic wave, or the like.

The thickness of the air permeable sheet is in the range of generally from 10  $\mu\text{m}$  to 3 mm, preferably from 50  $\mu\text{m}$  to 2 mm, more preferably from 75  $\mu\text{m}$  to 1 mm. If the sheet is too thin, it may not be able to function as a protective material and if it is too thick, the deodorant action may decrease.

The density of the air permeable sheet may range generally from 0.1 to 1.0  $\text{g/cm}^3$ , preferably from 0.2 to 0.9  $\text{g/cm}^3$ , more preferably from 0.3 to 0.8  $\text{g/cm}^3$ .

When the density is too high, deodorant action may decrease, and when it is too low on the other hand, protective function may decrease.

Examples of the air permeable sheet include fibrous sheets such as paper, unwoven fabric, cloth; nonfibrous sheets such as porous polymer film; and the like. The sheet form deodorizer can be lightened if a fibrous sheet is used.

5 The air permeable sheets may be applied on both sides of the deodorant polymer film to make the sheet form deodorizer. In this case, the air permeable sheet also serves as a supporting substrate for the deodorant polymer film. For example, as shown in Figure 1, a deodorant polymer sheet 101 may be sandwiched between two air permeable sheets 102, 102' each of which is a little larger than the deodorant polymer sheet 101, and circumferences of the sheets 102, 102' are  
10 bonded to make a sheet form deodorizer 100.

Also, a multi-layered film may be formed by piling up a deodorant polymer film and an air permeable sheet alternately (for example, the sum of the number of the deodorant polymer film and the air permeable sheet is from 3 to 11) so that the deodorant polymer film is arranged on each outer surface of both front and back  
15 sides.

Further, a deodorant polymer film may also be arranged as shown in Figure 2 to make a sheet form deodorizer. In Figure 2, number 201 indicates supporting substrate, number 202 indicates a deodorant polymer film, and number 203 indicates an air permeable sheet applied for protection. The distance (maximum  
20 distance) between the supporting substrate 101 and the back surface of the deodorant polymer film 202 represented by mark h in the figure is in the range of, preferably from 1 to 30 mm, more preferably from 2 to 15 mm. When the distance h is too small, improvement effect of deodorant action may be insufficient, and when it is too large on the other hand, the deodorant article may be too bulky to generate  
25 space saving effect.

The deodorant polymer film itself can also be made tacky. In such case, for example, an alkyl acrylate having 4 to 14 carbon atoms or an emulsion pressure-sensitive adhesive may be included into the monomer mixture used for polymerization of the deodorant polymer. The tacky deodorant polymer film can be  
30 directly attached to an adherend surface such as the inner surface of an accommodation container.

Further, when the deodorant polymer film is used in a public place, it is preferable to make the film transparent so as not to be visually recognized.

A decorated paper such as a poster and a calendar may be employed as the air permeable sheet, and the deodorant film may be applied on a back surface thereof.

5 As a result, a sheet form deodorizer having both decoration and deodorant ability is provided. A laminated structure in which the deodorant polymer film is interposed between two polymer films which do not have air permeability substantially may be formed, and thereby, a sheet form deodorizer having good storage stability is provided. In that case, at least one of the polymer film can be removed when it is  
10 used.

A procedure for evaluating the deodorant ability of the sheet form deodorizer is described as follows. The procedure for deodorizing is substantially the same as "self-standard of an aromatic and a deodorant for a public consumer" described in  
15 "Q & A The Safety Measures For Household Articles: You Can Completely Understand The Low For Regulating The Household Articles Which Contains A Harmful Substance" published by Gyosel K.K., June 20, 1991.

First, a sealed container having an odor atmosphere is provided. Specifically, a piece of glass is placed in a 6 liter desiccator. Then 50  $\mu$ l of an ethanol solution containing 0.5% by weight of ammonia is dropped on the glass as the odor  
20 substance, and the desiccator is closed with a lid and allowed to stand for 60 minutes. The ammonia concentration in the desiccator is measured by Detecting Tube No. 3 made by Gas Tech Corp., and was found to be about 13 parts per million (ppm).

A sheet form deodorizer having a suitable size (for example, 10  $\text{cm}^2$ ) is  
25 provided. It is then placed in a desiccator, and the odor atmosphere containing ammonia is filled in the desiccator according to the procedure as substantially the same as that described above, and is allowed to stand for 60 minutes. The ammonia concentration in the desiccator is then measured. The greater the deodorant ability of the sheet form deodorizer, the lower the ammonia concentration is from 13 ppm.

The sheet form deodorizer of the present invention has improved deodorizing effect since it contacts with a gas (usually air) containing an odor substance at a sufficient contact area.

Also, the sheet form deodorizer of the present invention enables maximum utilization of a space for accommodation and the like (space saving effect) since it can be adhered along a wall surface, ceiling surface and inner door surface. Further, the sheet form deodorizer of the present invention can be attached closely to a curved surface such as the surface of a dashboard of a car, and the like. Therefore the degree of freedom in selecting a place to put the deodorizer is large.

Further, the sheet form deodorizer of the present invention can be attached in a like manner to an inner surface of a garbage can or its lid, or an inner surface of a lid of a toilet bowl. In this case, since the sheet form deodorizer of the present invention can be placed near an odor source without disturbing the use of the garbage can or the toilet bowl, the deodorizing effect can be further enhanced.

### EXAMPLES

The following Examples and Comparative Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof.

#### Example 1

##### Preparation of a sheet form deodorizer

4 grams of 2-acrylamide-2-methylpropanesulfonic acid (hereinafter, referred to as "ACMPS"), 4 grams of deionized water, 2 grams of methyl polyethylene glycol methacrylate (available from SHIN NAKAMURA CHEMICAL INDUSTRY CORP. under the trade designation "NK ESTER" Product No. M90G, 0.06 g of 1,6-hexanedioldiacrylate and 0.1 g of a photopolymerization initiator (available from MERK CORP. under the trade designation "DAROCURE 1173") were added to a 10 ml glass vessel, and the vessel was rotated for stirring until a homogeneous solution was formed.

This solution was coated on a 50  $\mu$ m thick polyethylene terephthalate (PET) film which was subjected to a releasing treatment beforehand, and another 50  $\mu$ m thick PET film which was not subjected to releasing treatment, was applied on top

to make a layered body. Then, the layered body was irradiated by a ultraviolet light at a distance of 200 mm so that the total irradiation dose was 900 mJ/cm<sup>2</sup> using a 80 W UV lamp made by USHIO ELECTRIC Corp. By this irradiation, a sheet form deodorizer was obtained in which a transparent 100,  $\mu$ m thick deodorant polymer film was sandwiched by two PET films. The PET films are nonporous films.

The obtained deodorant polymer film had a deodorant polymer content of 60% by weight, and was a solid body which could maintain its film form stably even when subjected to work such as cutting. The content of the deodorant ethylenically unsaturated monomer ACMPS in the deodorant polymer was 66% by weight, and the content in the whole deodorant polymer film was 39% by weight.

The deodorant ability of the deodorant polymer film was evaluated according to the procedure for evaluating the deodorant ability of the sheet form deodorizer described above.

First, a piece of glass plate having a size of 7.5 cm x 2.5 cm x 1.0 mm was placed in a 6 liter desiccator, 50  $\mu$ l of an ethanol solution containing 0.5% by weight of ammonia as the odor substance was dropped on the glass plate. The desiccator was closed with a lid and was allowed to stand for 60 minutes. The ammonia concentration in the desiccator was measured by Detecting Tube No. 3 made by Gas Tech Corp., and was found to be 13 ppm.

The sheet form deodorizer was cut to a size of 10 cm<sup>2</sup>. One PET film was peeled off the deodorant polymer film, and the deodorant film was placed in the above-mentioned desiccator so that the surface of the film sufficiently contacted the gas. The desiccator was closed and allowed to stand for 60 minutes. The ammonia concentration in the desiccator was measured and found to be 0.20 ppm.

#### Example 2

A sheet form deodorizer was prepared in the same manner as Example 1 except that 2 grams of methyl polyethylene glycol methacrylate (available from SHIN NAKAMURA CHEMICAL INDUSTRY CORP. under the trade designation "NK ESTER", Product No. AM90G) was used instead of methyl polyethylene glycol, and 0.06 g of diethylene glycol dimethacrylate (available from SHIN NAKAMURA CHEMICAL INDUSTRY CORP. under the trade designation "NK

ESTER", Product No. 2G) was used instead of 1,6-hexane diol diacrylate. Further, the same deodorizing method as Example 1 was conducted with a resulting ammonia concentration of 0.23 ppm.

#### Example 3

5 A sheet form deodorizer was prepared in the same manner as Example 1 except that 2 grams of 4-hydroxybutyl acrylate was used instead of methyl polyethylene glycol methacrylate, and 0.06 g of diethylene glycol dimethacrylate (available from SHIN NAKAMURA CHEMICAL INDUSTRY CORP. under the trade designation "NK ESTER", Product No. 2G) was used instead of 1,6-hexane  
10 diol diacrylate. Further, the same deodorizing method as Example 1 was conducted with a resulting ammonia concentration of 0.22 ppm.

#### Example 4

2 grams of ACMPS, 2 grams of acrylamide, 6 grams of N, N-dimethyl  
acrylamide, 0.06 grams of diethylene glycol dimethacrylate (available from SHIN  
15 NAKAMURA CHEMICAL INDUSTRY CORP. under the trade designation "NK ESTER", Product No. 2G), and 0.06 g of a photopolymerization initiator manufactured by Merk Corp. under the trade designation "DAROCURE 1173" were added to a 10 ml glass vessel, and the vessel was rotated by stirring to make a homogeneous solution.

20 A sheet form deodorizer was prepared in the same manner as Example 1 except that the obtained homogeneous solution of Example 4 was used. The content of the deodorant ethylenically unsaturated monomer ACMPS in the whole deodorant polymer film was 20% by weight. Further, the same deodorizing method as Example 1 was conducted with a resulting ammonia concentration of 1.25 ppm.

#### Comparative Example 1

25 2 grams of ACMPS, 16 grams of deionized water, 1 gram of N-vinylpyrrolidone, 1 gram of polyethylene glycol diacrylate (available from KYOUEISHA CHEMICAL CORP. under the trade designation "LIGHT ACRYLATE", Product No. 14EG-A) and 0.08 g of a photopolymerization initiator  
30 (available from MERK CORP. under the trade designation "DAROCURE 2959")

were added to a 10 ml glass vessel, and the vessel was rotated for stirring to make a homogeneous solution.

5 A sheet form deodorizer was prepared in the same manner as Example 1 except that the obtained homogeneous solution of Comparative Example 1 was used. The content of the deodorant polymer in the obtained deodorant polymer film was 25% by weight. When the PET film was peeled off, a part of the polymerized substance was transferred to the peeled film. Namely, the deodorant polymer film was in the form of jelly, and film shape was not stable. Further, the same deodorizing method as Example 1 was conducted resulting in an ammonia  
10 concentration of 0.5 ppm. However, since the polymerization substance was adhered to both PET films, these were placed in the desiccator.

#### Comparative Example 2

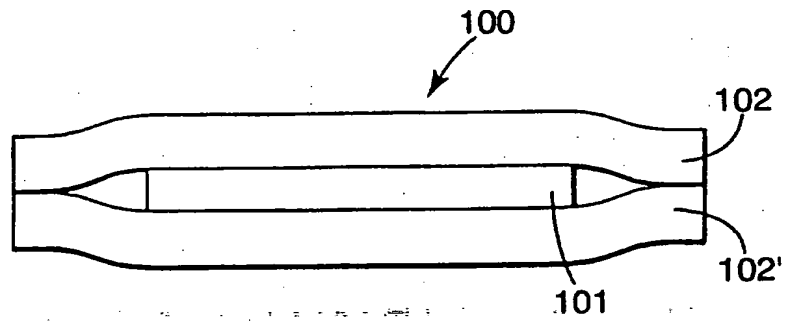
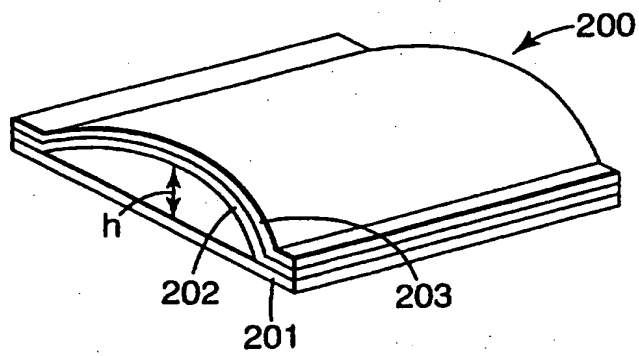
The same deodorizing method as Example 1 was conducted using 150 g of  
15 mixture of a vegetable extract having deodorant action and a water-absorptive gel resin (available from KOBAYASHI PHARMACY CORP. under the trade designation "MUKOU KUUKAN"). The ammonia concentration was found to be reduced to 7.0 ppm.

#### Comparative Example 3

20 The same deodorizing method as Example 1 was conducted using 44 grams of active carbon (available from WHITE HALL JAPAN CORPORATION under the trade designation "KIMUCO MAX REGULAR"). The ammonia concentration was found to be reduced to 1.3 ppm.

**WHAT IS CLAIMED IS:**

1. A deodorant polymer film comprising:
  - (a) 30 to 100% by weight of a deodorant polymer obtained by polymerizing 10 to 99% by weight of a deodorant ethylenically unsaturated monomer comprising a deodorant functional group and 1 to 90% by weight of a hydrophilic ethylenically unsaturated monomer having no deodorant functional group, based on a total weight of the deodorant polymer film; and
  - (b) 0 to 70% by weight of waterwherein said deodorant polymer is crosslinked and said polymer film is solid at ambient temperature.
2. A deodorant polymer film according to claim 1, wherein the deodorant ethylenically unsaturated monomer is included in an amount ranging from 10 to 90% by weight based on a total whole weight of the deodorant polymer film.
3. A deodorant polymer film according to claim 1 having a thickness of from 10  $\mu$ m to 5 mm.
4. A sheet form deodorizer comprising a substrate having at least one major surface and the deodorant polymer film according to claim 1 applied on the supporting substrate.
5. A sheet form deodorizer comprising a first air permeable sheet, the deodorant polymer film according to claim 1 applied on the first air permeable sheet, and a second air permeable sheet applied on the deodorant polymer film.

$\frac{1}{4}$ **Fig. 1****Fig. 2**

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/14293

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A61L9/01 A61L9/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	US 5 569 683 A (M.W. BOOTMAN ET AL.) 29 October 1996 see the whole document	1, 2
A	EP 0 631 788 A (NIPPON SHOKUBAI CO., LTD.) 4 January 1995 see claims	1-5
A	US 4 587 129 A (KLIMENT CHARLES K) 6 May 1986	
A	US 3 772 215 A (GOULD F ET AL) 13 November 1973	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

4 December 1997

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17/12/1997

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ESPINOSA, M

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/14293

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 4587129 A	06-05-86	NONE	
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